Relationship Between Cycling Performance and Structural Phase Transitions of $Li_{1+y}Mn_{2-y}O_4$ Cathode Materials Studied by Synchrotron X-ray Diffraction

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Introduction: Li_xMnO_4 based compounds with spinel structure have been widely studied as promising cathode materials for lithium ion batteries because of their low cost, low toxicity, and high energy density. Recent studies have focused on the problem of capacity fading of this material during cycling. Early ex situ x-ray diffraction studies of $Li_xMn_2O_4$ were performed by Ozhuku et al.[1]. They found that two cubic phases coexist for 0.60 > x >0.27, and a single cubic phase is present for 1.0 > x >0.6. When the cell is further discharged below 3.0 V to increase the x value in $Li_xMn_2O_4$ to the range of 1.0 < x < 2.0, the cathode material undergoes a phase transition to form a tetragonal structure. Xia and Yoshio[2] reported that this cubic to cubic phase transition can be suppressed in cathode materials which were prepared "lithium rich" (y=0.04 in $Li_{1+y}Mn_{2-y}O_4$) or "oxygen rich". They also claimed that this phase transition is one of the key factors responsible for the capacity fading of this material during cycling. Yang et al[3] proposed a three-cubic-phase model with two regions of two-phase coexistence for these $Li_{1+y}Mn_{2-y}O_4$ type materials when the battery cells were cycled between 3.5 to 4.5 V. This model was derived from *in situ* XRD studies on cells containing $Li_{1+y}Mn_{2-y}O_4$ type materials as cathodes and lithium foils as anodes. In this abstract, we report our studies on the relationship between the cycling performance and the structural phase transitions of these spinel materials during cycling in both 3V and 4V regions.

Methods and Materials: $Li_{1+y}Mn_{2-y}O_4$ (y=0 and 0.10) samples were synthesized by solid state reactions. Cathodes were prepared by slurrying $Li_{1+y}Mn_{2-y}O_4$ powder with 10% PVDF (KynarFlex 2801, Atochem), and 10% acetylene black (w/w) in a fugitive solvent, then coating the mix onto Al foil. After vacuum drying at 100 °C, the electrode disks (2.8 cm^2) were punched and weighed. The average weight of active material was 20mg. The electrodes were incorporated into the cells with a Li foil negative electrode, a Celgard separator and a 1 M $LiPF_6$ electrolyte in a EC:DMC (1:1 volume ratio) solvent (LP 30 from EM Industries Inc.). Mylar windows instead of beryllium windows were used in these in situ cells. *In situ* XRD spectra were collected on beam line X18A at National Synchrotron Light Source (NSLS) with radiation wavelength λ=1.195 Å. In order to record the phase transitions as detail as possible, the scan of 2θ angles were in the range of 43 to 53 degrees. Three Bragg peaks, (511), (440), and (531) for the cubic structure ($fd\bar{3}m$) were recorded for all the *in situ* XRD spectra in this region.

Results: In the *in situ* XRD spectra of stoichiometric lithium manganese oxide $Li_{1+y}Mn_{2-y}O_4$ (y=0), during the first charge from 3.5V to 4.5V at C/6 rate, three cubic structures, phase I, II and III can be identified. Nevertheless, due to the relatively wide range of the lattice constant change of both phase I and II, the two-phase co-existence region between phase I and II is not as clear as that between phase II and III. After discharging the same cell to 1.8 V through the whole 3V plateau, the phase transition from the cubic structured phase I to a tetragonal phase T was observed. The cell was subsequently charged back from 1.8 V to 4.5 V. After the transition from the tetragonal phase to phase I was completed through the 3 V plateau, the structure of the cathode consecutively transformed from cubic phase I to cubic phase II, then cubic phase III. Very interestingly, the changes in lattice constants of all three cubic phases are almost negligible during the second charge from 3.5 V to 4.5 V. The phase transition from phase I to Phase II and then to phase III can be clearly identified by the changes of the relative intensities of the Bragg peaks representing these three phases. This is quite different from that seen in the first charge and in a normal second charge from 3 V to 4.5 V, after a discharge limited to the 4 V plateau only. In that two cases, all three cubic phases have a "breathing range" in their lattice constants when lithium ion is deintercalated or intercalated from the cathode. Therefore, the phase boundaries are more or less smeared due to the overlaps of the breathing ranges of the neighboring phases, especially between cubic phase I and cubic phase II. Based on these results, we conclude that the structural changes of this cathode material through the 4 V plateau depend on the cycling history of the cell. The transition through tetragonal phase T may have created some kind of structural defects in the cathode material. These defects might restrict the breathing range of the lattice constants of the three cubic phases. These defects can severely restrict the breathing ranges of the three cubic phases and cause capacity fading.

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